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16. ABSTRACT

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SORPTION DYNAMICS OF HYDROPHOBIC POLLUTANTS IN SEDIMENT SUSPENSIONS

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Abstract—Sorption of hydrophobic organic chemicals in natural sediment suspensions was found to frequently require extended time periods (days to weeks) for complete equilibration. Sorption dynamics could be described by a two-compartment model that distinguished rapid or "labile" exchange (requiring at most a few hours to achieve) from highly retarded or "nonlabile" sorption requiring days to weeks to occur. In general, one-half or less of the total sorption was labile. For highly hydrophobic chemicals and high solid concentrations, the labile fraction decreased to 0.1 or less in some systems. The kinetic exchange constant for nonlabile sorption varied inversely with the sorption equilibrium constant. That is, the more highly sorbed chemicals sorbed more slowly. For some sediments, air-drying to facilitate sample transport or storage was found to result in formation of highly stable aggregates that severely altered sorbent availability to hydrophobic chemicals. An understanding of sorption dynamics is important in describing the fate of highly sorbed pollutants in aquatic systems.

Keywords—Sorption Kinetics Sediments Pollutants

INTRODUCTION

Examination of the literature on sorption reveals a great deal of confusion regarding the speed of attainment of sorption equilibrium. Sorption has often been described as rapid and readily reversible, with times to equilibrium of minutes to a few hours. Yet analytical chemists commonly have great difficulty extracting pollutants from soils or sediment samples. Highly sorbed chemicals frequently require lengthy extraction periods, multiple solvents, abrasive mixing techniques or a combination thereof for quantitative chemical recovery.

A concept long ascribed to by soil chemists (see Rao et al. [1] for a review of nonsingular sorption) and recently revamped to apply to sediment sorption [2] distinguishes equilibrium achieved in the forward direction (adsorption) from that achieved in a reverse direction (desorption). For the sorption of a hexachlorobiphenyl to various sorbents (sediment, clay, silica), DiToro and Horzempa [3] found that while the adsorption process was rapid (minutes to hours), the reverse process was slow because a significant portion of the sorbed chemical was highly "resistant" to release. Conventional partition coefficients were factored into reversible versus release-resistant components.

Karickhoff [4] reported a similar kinetic factoring for both adsorption and desorption of polynuclear aromatic hydrocarbons (PNA) on natural sediments, that is, 35 to 60% of the equilibrium sorption was achieved in minutes (mixing limited), with apparent equilibrium being reached after a few hours. In some systems in which sufficient accuracy in the sorption measurements did allow discernment of small changes in sorption over extended time periods, sorption continued to change (increase for adsorption, decrease for desorption) over periods of days to weeks. The maximal change in partition coefficient observed (relative to a 48-h measurement) was approximately twofold (pyrene, sediment 23). Also, a rather dramatic reduction in extractability of sorbed chemical was observed with increased incubation time. After short incubation periods (<5 min), essentially all (>90%) of the sorbed PNA could be recovered from the sediment suspensions by direct extraction with hexane for approximately 3 min. The fraction of sorbed chemical recovered by this brief extraction decreased rapidly over the first few hours of incubation (generally to <0.5) and, in most systems, continued to drop over the next few days, generally leveling out in the range

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of 0.2 to 0.4. All these findings are suggestive of an intraparticle process whereby chemical is slowly incorporated into either particle aggregates or sorbent components. If only changes in aqueous phase and/or sorbed phase concentrations are measured, then the process appears complete after a few hours, but in reality it may continue indefinitely.

Freeman and Cheung [5] ascribed nonlabile sorption behavior to physical incorporation of organic sorbates into natural organic matter, and suggested that the relative ease of chemical extraction by various solvents was related to the ability of a solvent to swell the humin-kerogen polymeric organic matter structure, thereby "effecting" sorbate release. Although this is consistent with a broad range of phenomenological observations concerning the uptake and chemical reactivity of sorbed chemicals, the observations of similar nonlabile sorption in "clean" mineral systems coupled with the recent implication of solids concentration in impacting sorbent availability [2,3] suggest that other processes are involved as well.

For sediment particles, several processes may contribute to what is collectively termed sorption kinetics. As mentioned, sorption may involve chemical movement into sorbent components (such as organic matter) or may involve uptake into porous aggregate structures. Aggregates in this context include any of a wide variety of naturally occurring particle assemblages, from loosely agglomerated sediment particles or clay mineral tactoids to more highly structured micelles or layered-lattice clay minerals. In some instances chemical uptake/release may be mediated by aggregate fracture/reformation. An underlying assumption is that no sediment particle structural changes are effected by the sorption of hydrophobic organic chemicals, in contrast to sorption of multivalent ionic species from which particle deformation or aggregation may result.

The kinetic description of sorption is further complicated by uncertainty regarding sediment particle structure. For uncharged organic pollutants, natural organic matter is considered to be the primary sorbent component, but the actual disposition of organic carbon in sediment particle structures is generally unknown. In addition, no data exist regarding the distribution (i.e., uniformity, anisotropy) of sorbed pollutants on or within the natural, organic sorbents.

The goals of this study were to identify the key sorbate/sorbent properties that significantly affect sorption kinetics and to develop models that quantify sorption in terms of readily available (or easily measurable) sorbate/sorbent properties. Because of the high degree of sorbent structural variability and uncertainty, and the process multiplicity involved, emphasis is placed on phenomenological descriptors for sorption kinetics that serve to discriminate among sorption events requiring minutes or days or months to occur. A molecular-level rationale concerning sorbent properties and structures and processes is used to suggest system variants for study or mathematical functionality for kinetic models, but no real effort is made to elucidate and describe in depth individual contributing processes. Special emphasis is given to highly hydrophobic chemicals that tend to be highly sorbed and for which sorption dynamics will probably affect chemical fate and/or transport in aquatic systems significantly.

SORPTION KINETIC MODELS

To date, little attention has been paid to developing a model of sorption kinetics in sediments or soils that recognizes highly retarded sorption behavior. Work by DiToro and Horzempa [3] to discriminate reversible from resistant sorption components can be construed as a quasikinetic model, but they did not address the temporal behavior of the resistant component. For trace metal sorption in marine sediments, Duursma and Bosch [6] found a highly retarded component which they ascribed to diffusive uptake into sediment particles. Their data, fitted to conventional diffusion models (porous spherical particles), gave effective diffusion coefficients of 10^{-12} to 10^{-15} cm^2/s. No attempt was made to characterize the active distribution volumes for metal uptake or to extrapolate measured diffusion coefficients to other sediments or metals.

In general, the use of molecular diffusion models requires boundary value specification (definition of diffusion volumes and chemical distribution on or within sediment particles) that is impractical in most pollutant fate modeling applications. One particularly simple model (infinite depth/planar source), however, offers considerable utility in examining laboratory data. If a pollutant that has been preequilibrated in a sediment suspension is desorbed under conditions involving continuous removal of solution-phase chemical (in these experiments via gas stripping), the sorbed chemical in the sediment behaves initially as an infinite depth/planar diffusion source (regardless of the number of independently contributing diffusion sources or the specific geometries of each source).

Under these conditions, temporal release of sorbed chemical into the water is given by

$$f_s(t) = k_s t^{1/2} \tag{1}$$

where $f_s(t)$ is the fraction of the total sorbed chemical released by time t and k_s is the diffusive release constant that sums the transport constants from contributing diffusion sources, incorporating structural characteristics of the source (i.e., active surface/volume ratios, porosity, etc.) as well as effective diffusion coefficients for the chemical in each source. (See Crank [7] for derivation of diffusion equations.)

A similar model describes chemical uptake by uncontaminated sediment from an infinite-strength solution source (i.e., not depleted by sorptive uptake):

$$f_u(t) = k_s t^{1/2} \tag{2}$$

where $f_u(t)$ denotes the fraction of the equilibrium uptake achieved by time t.

These diffusion models facilitate the examination of the impact of system variants (i.e., solids concentration, prepurge equilibration time, chemical/physical particle dispersal) on the transport constants, thereby providing some insight into the process(es) involved in chemical uptake/release. The boundary conditions for square-root temporal functionality, however, are too restrictive for general use in chemical fate modeling.

A more utilitarian approach to sorption for pollutant fate modeling is a two-compartment factoring of the sorbed state:

$$C \rightleftharpoons S_1 \rightleftharpoons S_2 \tag{3}$$

where C denotes solution phase chemical, and S_1 and S_2 denote two sorption compartments. These same symbols can be used to denote pollutant concentrations in the respective phases, with solution concentrations referenced to aqueous-phase volume and sorbed concentrations to total sorbent mass. If the two sorbed states S_1 and S_2 are assumed to differ only in kinetics of access from the aqueous phase, then $S_1^e/X_1 = S_2^e/(1 - X_1)$ at equilibrium (indicated by superscript e), where X_1 denotes the fractional sorbent mass in the labile component S_1. Access to and from the nonlabile state S_2 is given by

$$\frac{1}{1 - X_1}\frac{dS_2}{dt} = -k_2\left[\frac{S_2}{1 - X_1} - \frac{S_1}{X_1}\right] \tag{4}$$

where k_2 is the kinetic constant for accessing compartment S_2. If chemical exchange between the solution phase and S_1 is assumed to be sufficiently fast to maintain equilibrium between these two phases, sorption can be described with one kinetic coefficient (k_2), and for closed systems (i.e., no chemical attenuation) is given by

$$\begin{aligned}\frac{\theta C - RT}{\theta C^\circ - RT} &= \frac{\rho S - (1 - R)T}{\rho S^\circ - (1 - R)T} \\ &= \frac{\rho S_1 - X_1(1 - R)T}{\rho S_1^\circ - X_1(1 - R)T} = \cdots \\ &= \frac{\rho S_2 - (1 - X_1)(1 - R)T}{\rho S_2^\circ - (1 - X_1)(1 - R)T} \\ &= \exp\left[-k_2\frac{R_1}{R}(t - t_0)\right]\end{aligned} \tag{5}$$

where T is the total pollutant concentration ($T \equiv \theta C + \rho S$); S is the total sorbed pollutant concentration ($S = S_1 + S_2$); θ is the volumetric water content (aqueous phase volume relative to total volume); ρ is the solids concentration (solids mass per unit suspension volume); R and R_1 are retardation parameters defined by ($1/R \equiv 1 + \rho/\theta\ K_p$ and $1/R_1 \equiv 1 + X_1\ \rho/\theta\ K_p$); and K_p is the equilibrium partition coefficient ($K_p = S^e/C^e$). Concentrations with superscript ° denote values at some initial time t_0, taking into account equilibrium of C and S_1. For example, if pollutant is added to a suspension of uncontaminated sediment, then $\theta C^\circ = R_1 T$, $\rho S_1^\circ = (1 - R_1)T$, $\rho S_2^\circ = 0$ and $\rho S^\circ = (1 - R_1)T$. On the other hand, for the suspension of contaminated sediment in uncontaminated water, $\theta C^\circ = X_1 R_1 T$, $\rho S_1^\circ = X_1(1 - R_1)T$, $\rho S_2^\circ = (1 - X_1)T$ and $\rho S^\circ = (1 - X_1 R_1)T$. (See Karickhoff [4] for a more complete derivation.)

For open systems with initial boundary conditions as described previously for diffusive release/uptake (i.e., for release, pollutant preequilibration with the sediment followed by desorption under continuous stripping of aqueous-phase chemical, and for uptake, chemical uptake by uncontaminated sediment from a constant aqueous-phase source), the two-compartment model gives, for $f_r(t)$ and $f_u(t)$:

$$f_r(t) \text{ or } f_u(t) = 1 - (1 - X_1)\exp(-k_2 t)\ . \tag{6}$$

With regard to the temporal range of applicability, the two-compartment model (Eqns. 5 and 6)

describe kinetically the nonlabile or resistant sorption component and, therefore, are long-time descriptors, valid for time frames comparable to $1/k_2$ or longer. It should be pointed out that this series model is kinetically indistinguishable from a parallel model ($S_1 \rightleftharpoons C \rightleftharpoons S_2$) as long as equilibrium is assumed between S_1 and C. That is, Equations 5 and 6 describe either model. The series model more aptly distinguishes sorption sites differing primarily in diffusion path lengths for access to and/or from bulk water, whereas the parallel model distinguishes sites accessed by routes differing in effective diffusion coefficients. The series model is tacitly used herein to differentiate access to S_1 and S_2, but a parallel model would suffice.

MATERIALS AND METHODS

With the exception of the Oconee River sediment, the sediments and soils used in this study were from a set collected and characterized by Hassett et al. [8]. Table 1 gives a brief description of these samples. The Oconee River sediment was collected by local U.S. Environmental Protection Agency (EPA) personnel. Organic carbon analysis on this sediment was performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Particle size analysis was by sedimentation as described by Karickhoff et al. [9]. Reagent-grade pyrene, pentachlorbenzene and hexachlorobenzene (K and K Laboratories) were used as received. Trifluralin was an analytical reference standard (EPA, Research Triangle Park, NC). Tenax resin (60/80 mesh) was used as received from Altech Associates.

Spiking of test chemicals into sediments

The test chemicals were plated out of isooctane standard solutions onto the walls of glass Erlenmeyer flasks. Sediment/soil suspensions were added and the samples shaken (wrist action or platform shaker) for prescribed incubation periods. The quantities of chemicals introduced were adjusted so as to produce solution-phase concentrations (at equilibrium) equal to or less than half-saturation (i.e., water solubilities) for each chemical. Previous work with these types of chemicals [9] determined that this was sufficient to assure linear sorption behavior.

Purge-induced desorption

Sediment suspensions containing the test chemicals were placed in specially fabricated purge cells (Fig. 1) and desorption was induced by continuously stripping the chemical from the aqueous phase. The cell bottoms were glass frits (fine or medium porosity), which served to distribute the purge gas uniformly across the cell and to sustain sediments in suspension for extended periods at minimal flow rates. The cell volume was adjustable (200 to 1,000 ml) with the insertion of glass sleeves of the appropriate length to accommodate the desired volume. Head space was kept at a minimum to lessen void-space sink potential and transport resistance for sparged chemicals.

Table 1. Sediments and soils: Physical properties

Sediment number	Location	% organic carbon	pH (1:1)	% silt	% clay
4	Missouri River Stanton, ND	2.07	7.79	41.8	55.2
6	Missouri River Big Ben Lake, SD	0.72	7.83	31.2	68.6
8	Missouri River Onawa, IA	0.15	8.32	10.7	6.8
9	Loess Soil Turin, IA	0.11	8.34	75.6	17.4
13	Ohio River Ceredo, WV	3.04	6.90	27.1	52.6
26	Mississippi River McClure, IL	1.48	7.75	55.4	37.1
B-2	Small Stream Watkinsville, GA	1.21	6.35	13.9	18.6
OR	Oconee River Athens, GA (suspended sediment)	1.52	6.47	31.1	37.1

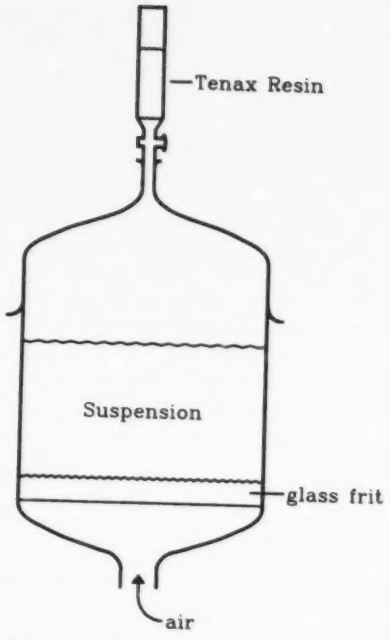

Fig. 1. Gas purge cell for desorption studies.

The purge gas was laboratory air collected (oil-less compressor), cleaned (brass frit, paper filter, charcoal, tenax resin), saturated with water and three-stage-flow regulated. Air flow rates (0.2 to 10 L/min) were adjusted to keep the sediment suspended and to isolate kinetically the desired process. Sparged chemicals were collected on tenax resin. Sampling intervals (i.e., resin column changes) were chosen to provide the desired temporal resolution in the chemical release profile. The test chemicals were recovered from the resin by reverse-flow solvent elution (1 pore volume acetone or methanol followed by 2 pore volumes isooctane). Water was added to the eluate to remove the polar solvent and the test chemicals were quantified in the isooctane phase [UV absorption spectroscopy for pyrene, electron capture gas chromatography (SE-30 gas chrom Q column) for the other test chemicals].

All purge experiments were run in duplicate or triplicate. Reproducibility between replicates was very good. Rarely would purge responses for any given sample interval differ by more than 10% among replicates.

Chemical analyses in sediment suspensions

Chemical concentrations in the water phase were determined (in triplicate) just prior to purge, and total chemical (sorbed plus solution phases) was determined at the termination of each experiment.

The test chemicals were extracted from sediment suspensions with an acetonitrile/isooctane solvent mixture (1:1, v/v). Samples were sonicated for 8 h (Cole Palmer ultrasonic bath) with vortex-mixing every 2 h. The test chemicals were quantified in the isooctane phase as specified above for the purge samples. For chemical analyses in individual phases, the suspensions were phase-separated by centrifugation (20,000 rpm, 60 min, RC2-B rotor) in stainless steel tubes. Test chemicals in the sediment phase were extracted with a solvent mixture of distilled water, acetonitrile and isooctane (6:1:1, v/v). Samples were mixed and test chemicals quantified as specified previously for sediment suspensions. Test chemicals in the aqueous phase were extracted with an acetonitrile/isooctane mixture (1:1, v/v), vortex-mixed, sonicated for 2 h and quantified in isooctane as described above. Considerable variation in aqueous phase analyses occurred among replicates, especially for the more hydrophobic chemicals (i.e., hexachlorobenzene). The coefficient of variation among replicates (standard deviation/mean) was frequently as large as 0.3 at sub-parts per billion (i.e., μg/L) levels.

RESULTS AND DISCUSSION

Methodology: Impact on sorption measurements

For highly sorbed chemicals, the observed kinetics for chemical uptake or release by sediments can be very dependent on experimental methodology. Typical methods of introducing a chemical into sediment involve either the dumping of sediment (dry or suspended) into an aqueous solution of the test chemical or injection of the chemical, dissolved in a small quantity of water-miscible solvent, into a sediment suspension. For systems where $\rho/\theta\ K_p \gg 1$, these methods produce a highly disproportionate loading of a small fraction of the total sediment particles and as a result may bias uptake kinetics significantly. For these systems, chemical introduction by a diffuse source, such as plating (as in these experiments) or gaseous perfusion, produces a much more uniform chemical distribution among suspended particles. With these methods, a steady state in chemical

concentration in the water is typically achieved rapidly, which allows the examination of sorption uptake under constant source conditions (i.e., Eqn. 2).

In the case of desorption, again, conventional methods of inducing chemical release tend to bias release kinetics significantly. Typically, to effect desorption, preequilibrated sediment/chemical suspensions are either diluted with clean water or are phase-separated (via centrifugation, filtration or settling) and the sediment resuspended in clean water. With these methods, the initial release kinetics is frequently dominated by solids dispersion and typically follows zero-order kinetics with respect to the sorbed chemical concentration. The gas-stripping techniques used herein obviate the solids perturbation problems but are applicable only to a fairly narrow range of sediment/chemical systems. In general, purge techniques can be applied with varying degrees of success to most uncharged, nonpolar organic chemicals.

For halogenated hydrocarbons, the entire desorption release profile [$0 < f_r(t) < 1$] can frequently be followed, whereas for nonhalogenated hydrocarbons, desorption kinetics can be resolved in the purge response only during the latter stages of release ($f_r > 0.5$).

It should be emphasized that purge/release profiles are useful not only as a means of characterizing desorption, but as a sensitive indicator of adsorptive approach to equilibrium as determined by changes in the release profile with increased prepurge incubation time.

The majority of the sediments used in this study were air-dried to facilitate transport and storage. In general, drying did not significantly alter the sorption properties (kinetic or equilibrium) on rewetting (approximately 5 d prior to use). For some sediments, however, air-drying resulted in the formation of highly stable aggregates that did not disperse under conventional mixing, even after extended periods (weeks). Chemical uptake by these sediments showed a major portion of the sorbent to be unavailable after several months of incubation. In the Illinois sediments, Nos. 5 and 23 showed this artifact on the sorption properties, especially for large sorbate molecules (such as four- or five-ring condensed-ring hydrocarbons or highly halogenated aromatic compounds).

Short-term sorption kinetics

The initial stage of purge-induced release of sorbed hexachlorobenzene, pentachlorobenzene and trifluralin from preequilibrated sediment suspensions followed conventional diffusion kinetics. That is, when the chemicals were equilibrated with sediment suspensions and subsequently purged under conditions that maintained solution-phase chemical concentrations near zero, the early portion of the release profile (i.e., $f_r < 0.5$) followed Equation 1 (Fig. 2). The complementary experiment for chemical uptake involved holding the chemical concentration in solution constant and measuring sorbed concentrations at various incubation times. In this case, although measurement precision comparable to desorptive release was not achievable, uptake generally followed a comparable planar diffusion model (Eqn. 2 and Fig. 3). Uptake constants, however, always exceeded those for release, typically by as much as a factor of 2. This is typical of highly retarded diffusion phenomena and may derive from the failure to achieve true sorption equilibrium prior to desorption.

The magnitude of the observed kinetic constants (0.1 to 1.0 $d^{-1/2}$) reflects a highly retarded diffusional process. For example, if sorption is presumed to involve diffusive movement into 10-μm spherical particles, these kinetic coefficients correspond to effective diffusion coefficients on the order of 10^{-11} to 10^{-13} cm^2/s (compared with molecular diffusion coefficients in water of 10^{-6} cm^2/s). This clearly suggests that sorption involves sites or sorbent components that are not contiguous to bulk water. The similarity in magnitude of these diffusion coefficients to those observed by Duursma et al. [6] for radionuclide uptake by sediments is also noteworthy.

Experimental limitations prohibited the measurement of these early release/uptake profiles for all but a few chemical/sediment systems. Two important trends, however, were discernible. First, the kinetic coefficients (k_s) generally varied inversely with equilibrium K_p. This trend was observed for a given chemical on different sediments and for different chemicals on a given sediment, and is consistent with increased resistance to intraparticle transport with increased sorption and/or molecular size. Second, for many sediments, the transport coefficients were dependent on the solids concentration. For highly cohesive solids (such as sediment 13, Table 1) diffusive transport coefficients increased significantly at lower solids concentrations (Fig. 4). In some cases, the addition of dispersants had an effect similar to lowering the solids concentration, suggesting the phenomenon to be associated with sediment aggregates which disperse on dilution or in the

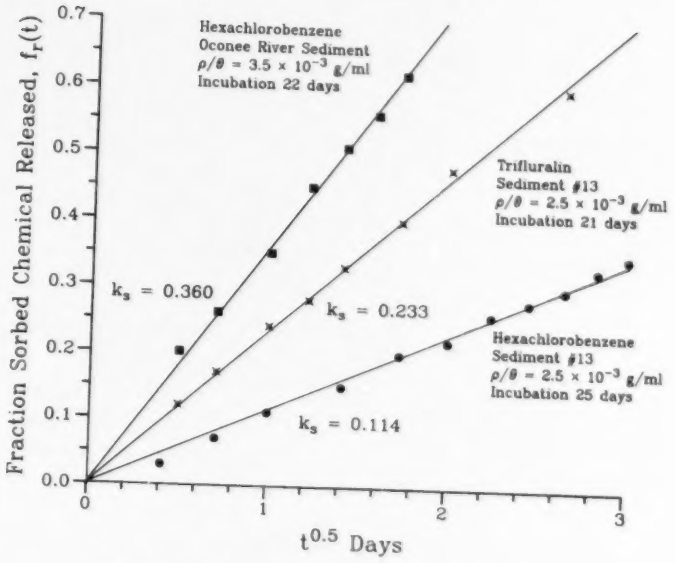

Fig. 2. Initial desorptive release induced by gas purge.

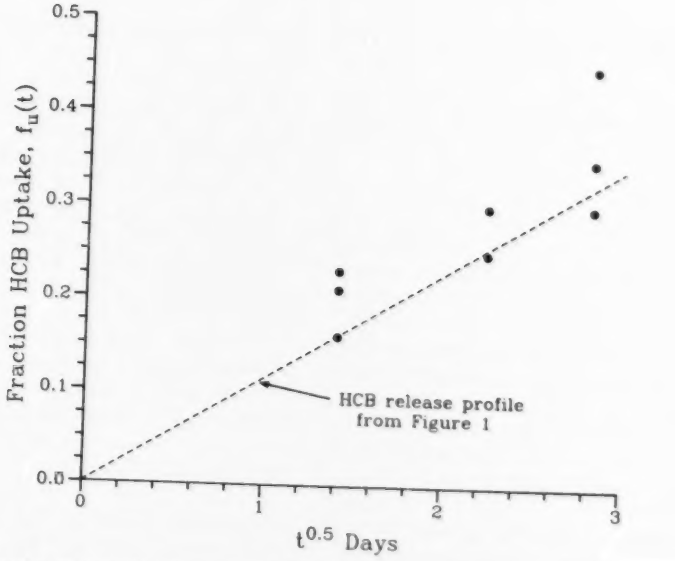

Fig. 3. Sorptive uptake of hexachlorobenzene (HCB) under constant source conditions (sediment No. 13; $\rho/\theta = 2.5 \times 10^{-3}$ g/ml).

presence of dispersants. For local sediments (non-cohesive, low in carbon, with kaolin-dominated clays), a minimal effect of solids concentration on release kinetics was observed.

Long-term desorptive release

Fixed geometry diffusion models [7] were examined for the entire release profile ($0 < f_r < 1$), but

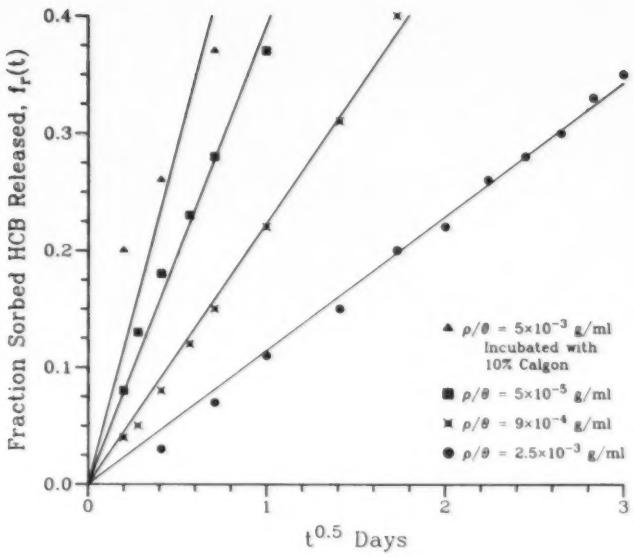

Fig. 4. Effect of solids concentration on purge-induced hexachlorobenzene (HCB) release (sediment No. 13).

no model was found to be generally applicable (i.e., for different chemicals, sediments, solids concentrations, etc.). Sediment particle size and structural variability (inherent in a given sediment or between sediments) seemed to preclude the general applicability of any particular model.

If a logarithmic plot of the fraction of the initially sorbed chemical remaining $[1 - f_r(t)]$ versus purge time (Fig. 5) is examined, the slope at any given time corresponds to a desorption rate constant. For such plots, a monotonic decrease in slope with time was characteristically observed, indicative of a continuously increasing resistance to desorption. The change in slope over the entire release profile was typically in excess of one order of magnitude, negating the use of a first-order model containing a single desorption rate constant. The greatest changes in slope (or release constant) occurred during the early stages of release (depletion of the near-surface sorbed material) and again during the final stages of chemical release. The final portion of the sorbed material [10% (m/m)] tended to "bleed" very slowly, especially from highly cohesive sediments, in some cases requiring more time for release than the first 90%. It should be emphasized, however, that, in all systems studied, sorbed chemicals could be recovered quantitatively via purge, that is, no irreversible binding was observed.

The purge profiles suggest that the major portion of the chemical release (ignoring the final bleed component) could be described by a two-compartment linear model (as described previously, Eqn. 3) that distinguishes a labile or rapid sorption component (requiring at most a few hours to achieve) and a nonlabile or resistant component. Because the time frame for the labile process was short relative to typical temporal resolution in environmental modeling, equilibrium was assumed for this component $(X_1 K_p)$. The nonlabile component was treated as a first-order process (Eqn. 4) with no directional distinction (chemical uptake versus release). As was found in a previous study with chemicals sorbed to a lesser extent [4], the rate constant k_2 was inversely correlated with sorption K_p (Fig. 6 and Table 2). When the data collected in the two studies were combined, an equation relating the characteristic time $(1/k_2)$ for nonlabile sorption to K_p was found that seemed to hold over a range of characteristic times in excess of three orders of magnitude (hours to months):

$$1/k_2(\text{h}) \approx 0.03\ K_p \text{ (correlation coefficient} = 0.87) \quad (7)$$

Individual data deviate from this equation by as much as a factor of 3, but the relationship clearly defines the appropriate time frame for nonlabile sorptive events (minutes vs. hours vs. days). These

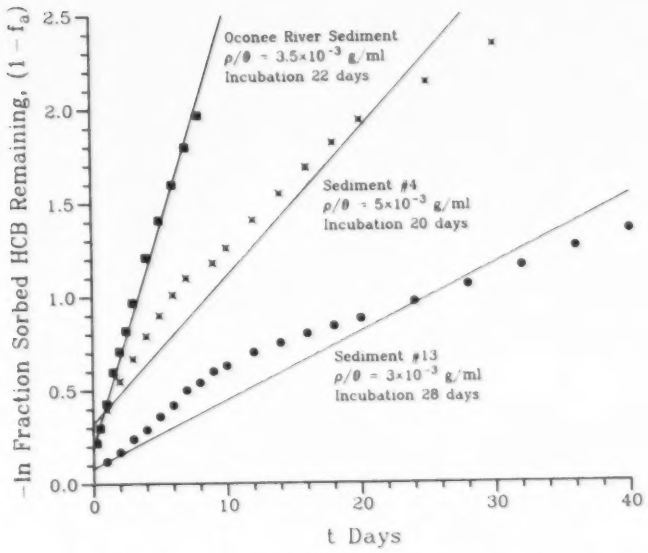

Fig. 5. Long-term release of hexachlorobenzene (HCB) under continuous gas purge.

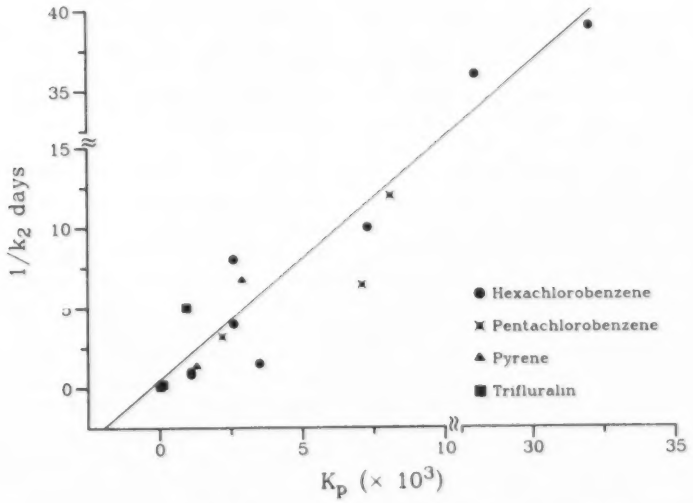

Fig. 6. Dependence of nonlabile release constant (k_2) on sorption equilibrium constant (K_p).

data suggest times to reach equilibrium on the order of 0.1 K_p (h). For chemical/sediment systems with $K_p > 10^5$, equilibration times in excess of 1 year would be expected. It should be emphasized that no systems of this type were studied, but many high-profile pollutants should fall in this category (e.g., polychlorinated biphenyls with six or more chlorines, or condensed-ring aromatic hydrocarbons with five or more rings).

In this work, the labile component was quantified operationally by extrapolating the log-linear portion of the fractional release profile to zero time (Fig. 5). Typically, 25 to 60% of the total sorbed chemical was labile. For systems in which a very

Table 2. Desorption kinetics: Two-compartment model

Chemical	Sediment number	Solids concentration (g/L)	Equilibration time (d)	Equilibrium constant (K_p)	Labile fraction (X_1)	Exchange constant (k_2) (d^{-1})
Hexachlorobenzene	4	5.0	20	7,300	0.24	0.10
	8	32	18	1,100	0.48	1.2
	9	10	18	1,100	0.48	1.0
	13	3.0	28	32,000	0.11	0.026
	13	2.5	25	28,000	0.15	0.028
	26	25	28	2,600	0.16	0.25
	B-2	13	20	3,500	0.28	0.67
	OR	3.5	22	2,600	0.35	0.13
Pentachlorobenzene	13	2.5	28	8,100	0.22	0.083
	13	3.5	15	7,100	0.24	0.16
	26	7.5	28	2,200	0.29	0.31
Pyrene	13	0.4	21	2,900	0.36	0.15
	26	0.5	15	1,300	0.59	0.75
Trifluralin	6	18	10	120	0.47	4.8
	9	10	10	23	0.50	12.5
	13	2.5	21	950	0.22	0.2

B-2, sediment from Small Stream, Watkinsville, GA; OR, sediment from Oconee River, Athens, GA (see Table 1).

large proportion of the total chemical was sorbed (≥99%), however, the labile component decreased to as little as 10%. As would be expected from the behavior of the diffusive transport coefficient for early release (k_s), X_1 tended to decrease with either increasing K_p or increasing solids concentration (see Fig. 7). This phenomenological behavior derives in part from the operational time-frame qualification for labile processes. Since the diffusive transport coefficient k_s varies inversely with K_p, the fractional sorbent volume that is accessible (for chemical uptake/release) in a bounded time frame should be inversely correlated with K_p. As discussed previously for k_s, the solids-concentration dependence of X_1 is suggestive of particle aggregation, but the existence of such structures was not confirmed in this study. DiToro (manuscript in preparation) observed a similar dependence of readily reversible sorption on the product $\rho/\theta K_p$.

It should be pointed out that the labile fractions (X_1) and kinetic constants (k_2) for desorption are for systems at (or near) equilibrium at the time of purge-induced desorption. If desorption is induced after brief incubation, the aforementioned trends for the two-compartment model coefficients may change rather dramatically. Typically, for sorption reversal after brief incubation ($t \ll 1/k_2$), the observed labile fraction increases with a concomitant increase in the apparent exchange constant k_2. Also, the solids-concentration dependence of k_2 is frequently inverted (i.e., k_2 increases with increasing solids concentration). This behavior derives simply from disequilibrium in the diffusive uptake. The two-compartment model assumes isotropic distribution of sorbate in both sorption compartments (S_1 and S_2) at all times and therefore does not describe sorption reversal after time periods $\ll 1/k_2$.

CONCLUSIONS

Although sorption to soils and sediments is frequently described as fast and readily reversible, true sorption equilibrium required, in some cases, days to weeks to achieve. The nonlabile sorption character appeared to derive from a nonsurface sorbent, accessed by highly retarded molecular diffusion. A two-compartment model was used to describe quantitatively the kinetics of chemical uptake/release. This model distinguishes rapid sorption processes (requiring at most a few hours to occur) from chemical exchange requiring extended periods (several days to months) to achieve. The fraction of the total sorption that was labile was typically 0.25 to 0.6, but decreased to 0.1 or less for highly sorbed chemicals at high solids concentrations ($\rho/\theta K_p > 100$). For large hydrophobic molecules (such as hexachlorobenzene), the labile fraction did not approach unity at low solids concentration (50 mg/L or less), indicative of a nonsurface sorption component in highly dispersed systems. The kinetic exchange constant for nonla-

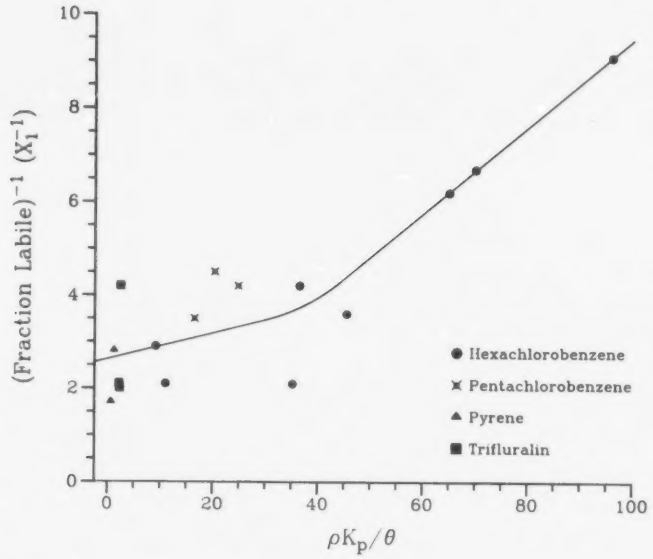

Fig. 7. Dependence of labile sorption (X_1) on solids concentration (ρ) and sorption equilibrium constant (K_p).

bile sorption (k_2) varied inversely with sorption K_p, consistent with sorptive resistance to chemical transport to nonsurface sorption components.

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